CONDENSED PYRIDINES.

COMMUNICATION 7.* PREPARATION AND CONVERSIONS OF 6-ARYL-3-CYANO-2(1H)-PYRIDINETHIONES AND CRYSTAL STRUCTURE OF 2,2'-BIS[6-(2,4-DIMETHOXYPHENYL-3-CYANO-2-PYRIDINYL) DISULFIDE

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In the course of our investigation into the reactions of unsymmetrical 1,3-dicarbonyl compounds with acetamides we have studied the reaction of sodium 3-aryl-3-oxo-1-propen-1-olates (Ia-c) with cyanothioacetamide. Successive treatment of the salts (Ia-c) in ethanol with acetic acid and cyanothioacetamide (II) leads to the formation of 6-aryl-3-cyano-2(1H)-pyridinethiones (IIIa-c).



 $Ar = C_{6}H_{5}(a), \ 4\text{-}ClC_{6}H_{4}(b), \ 2,4\text{-}(CH_{3}O)_{2}C_{6}H_{3}(c) \ (1), \ (111).$

When a solution of the pyridinethione (IIIc) in acetic acid is kept in air for several days the disulfide (IV) is formed. Alkylation of (IIIa) with phenacyl bromide or allyl bromide in DMF in the presence of KOH proceeds under mild conditions at the sulfur atom exclusively forming thiopyridines (V) and (VI). From (V), and also by a single-stage synthesis from (IIIa) and phenacyl bromide in the presence of KOH according to the Thorpe-Ziegler reaction [2], one obtains 3-aminothieno[2,3-b]pyridine (VII).

*For previous communications, see [1].

A. M. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 140-145, January, 1988. Original article submitted June 30, 1986. By the action of bromine on a solution of (VI) in chloroform one obtains an intramolecular quaternization product — the bromide of 3-bromomethyl-5-phenyl-8-cyano-2,3-dihydrothiazolo[3, 2-a]pyridine (VIII) which is converted to the more stable perchlorate (IX) on treatment with perchloric acid in acetic acid.

Attempts to prepare the perchlorate of thiazolo[3,2-a]pyridine (X) by intramolecular quaternization of (VI) by the action of perchloric acid ended in failure, probably associated with the protonation of the pyridine ring as a result of its quite high basicity. At the same time, when an equimolar quantity of bromine is added to the mixture, quaternization of (VI) to (IX) occurs. The results obtained support those of [3] in that the intramolecular quaternization of 2-allylthiopyridines to thiazolo[3,2-a]-pyridinium cations proceeds via the generation of an electrophile on account of heterolytic rupture of the double bond of the allyl group of compound (VI). Subsequent closure of the ring with the formation of compound (VI). The possibility that electrophilic rupture of the double bond of the allyl group and intramolecular quaternization take place simultaneously is not excluded. The formation of only one isomer of the cation of compounds (VIII) or (IX) is in agreement with the results of the X-ray structural analysis of thiazolo[3,2-a]pyridines [1, 3].

The structure of the compounds prepared was confirmed by physical and chemical examination. In the conversion of (VI) to (VIII) and (IX) a reduction in the intensity of the CN absorption band is observed in the IR spectrum and a shift of $\Delta v 18-20 \text{ cm}^{-1}$ to higher frequency; this is connected with the delocalization of the positive charge on the pyridine fragment of (VIII) and (IX). In the PMR spectrum of the salts (VIII) and (IX) there are multiplets due to the protons of dihydrothiazole which are characteristic for 2,3-dihydrothiazol[3,2-a]pyridinium cations [1]. The doublet for the C⁷H proton of compounds (VIII) and (IX) is shifted downfield by 0.76 ppm in comparison with the C⁶H proton of (VI) while the shift in the signal for the C⁶H protons of (VIII) and (IX) in comparison with C⁵H of (VI) is negligible. Such polarization of the protons in (VIII) and (IX) is evidently connected with nonuniform redistribution of charge in the pyridine ring.

For final confirmation of the position of the aryl substituent on the pyridine nucleus of (IIIa-c) the disulfide (IV) was examined by x-ray diffraction. It was established that the aryl substituent in (IV) is found in the 6-position, not in the 4-position, of the pyridine ring (Fig. 1), that is, the compound studied is 2,2'-bis[6-(2,4-dimethoxyphenyl)-3-cyanopyrid-yl-2] disulfide and is one of the symmetrical "aromatic" disulfides (SADS) RSSR in which the disulfide bridge connects sp²-hybridized carbon atoms of the R-groups. The fundamental geometrical parameters of SADS are the torsion angles of $C(N)CSS(\tau)$ and $CSSC(\varphi)$ and the lengths of the S-S and C-S bonds. Some empirical relationships between these parameters are considered in [4].

The C-S distances in axial and equatorial SADS are less than the average values for the length of single C-S bonds in aliphatic disulfides (1.817(5) Å [5]), the bond length C_{sp2} -S in equatorial SADS (1.767(10)-1.797(9) Å) being somewhat greater than in axial SADS (1.744(5)-1.770(7) Å) [4]. In particular, in axial bis(2,8-diphenylindolizine-3-yl) disulfide (XI) [6] the lengths of the C-S bonds are reduced to 1.697(3) and 1.715(3) Å (average 1.71(1) Å) which, in the authors' opinion, results from n - σ^* interaction with shift of the electron density of the unshared electron pair of the S atom to the antibonding orbitals of the R group bonds. In (IV) the lengths of the C-S bonds (1.788(2) and 1.788(2) Å) have values characteristic for equatorial SADS, as in the related molecules bis[(6-adamantyl-1)-3-cyanopyridyl-2] disulfide (XII) (1.772(6) and 1.787(6) Å) and bis(pyridyl-2) disulfide (XIII) (1.785(2) and 1.785(2) Å) [8].

The molecule (IV), which has electron-acceptor (CN) substituents in the ortho-position on each of its pyridine rings and the torsion angles of which are small (τ (N¹C²S¹S^{1'}) = -0.6(2)[•] and τ (N¹'C²'S¹'S¹) = -19.3(2)[•]), belongs to the class of equatorial SADS, as also do compounds (XII) and (XIII) which are related to (IV) and have $\tau = -31.5(3)$, 16.8(5)[•] and $\tau = 5.1$, 10.2[°], respectively.

The torsion angle about the S-S bond (φ) is found in the range 66-110°, in the majority of cases close to 90 ± 10° [8]. Such an approximately orthogonal arrangement leads to weak repulsion of the unshared electron pair of the S atom. Pronounced deviation of the angle from 90° in the axial disulfide (XI) ($\tau = 80.6(1)$ and 79.6(2)°, $\varphi = 62.8(2)$ °) leads to a marked increase in the S-S distance to 2.141(1) Å in comparison with S-S distances in equatorial (1.999-2.550, av. 2.03 Å) and axial (2.059-2.108, av. 2.08 Å) SADS. The values of the torsion angle φ in (IV) and in (XII) and (XIII) (-83.5(2), 80.8(5), and 87.1°, respectively) and also for the S-S bond lengths (2.015(1), 2.022(3), and 2.016(2) Å, respectively) are normal for equatorial SADS.

The inverse relationship between the lengths of the C-S and S-S bonds in SADS was noted in [4]: in equatorial SADS one observes a certain shortening of S-S bonds and lengthening of C-S bonds in comparison with axial SADS.

The bond angles at the S atoms in (IV), equal to 104.3(1) and $103.3(1)^{\circ}$, are in good agreement with those observed in other organic disulfides where they amount to $98-106^{\circ}$ in accordance with the supposed p³-configuration of the S atoms in SADS [6].

The substituted benzene rings in the molecule of (IV) are in fact coplanar with the pyridine (torsion angles N¹C⁶C⁸C¹³ and N¹C⁶'C¹³' are -8.3(3) and -3.4(3)°, respectively) and the methoxy groups with the plane of the benzene rings (torsion angles C⁶C⁹O¹C¹⁴ = 174.7(4)°, $C^{10}C^{11}O^2C^{15} = 4.2(4)°$, $C^{8'}C^{9'}O^{1'}C^{14'} = 172.4(4)°$, and $C^{10'}C^{11'}O^{2'}C^{15'} = 2.3(4)°$). Thus, in the molecule of (IV) it is possible to isolate two approximately planar fragments united by a disulfide bridge.

The short, nonvalence, intramolecular contacts $S^1...N^1$ 3.064(2) Å and $S^1'...N^1$ 3.030(2) Å should be noted; the sum of the van der Waals raddi of S and N atoms is 3.35 Å [9]. This evidently influences the rotation of the pyridine rings about the corresponding CSS planes. Analogous nonvalence contact is also observed in (XII) and (XIII).

According to the criteria for the existence of C-H...O type hydrogen bonds [10], one can conjecture that in (IV) there is intramolecular hydrogen bonding between the O¹ and O¹ atoms of the methoxy groups and the H⁵ and H⁵' atoms on the C⁵ and C⁵' atoms of the heterocycles (O¹...C⁵ and O⁴⁺...C⁵⁺ 2.804(3) and 2.788(3) Å, O¹...H⁵ and O¹⁺...H⁵' 2.14(2) and 2.15(2) Å, C⁵-H⁵ and C⁵'-H⁵' 0.96(2) and 0.93(2) Å, angles C⁵-H⁵...O¹ and C⁵'-H⁵'...O¹⁺ 125(2) and 125(2)°, C⁹-O¹...H⁵ and C⁹⁺-O¹⁺...H⁵' 106.3(7) and 106.5(7)°).

In the crystal of (IV), a series of intermolecular contacts of S...C and C.₈.C type are observed, less than or close to the sum of the van der Waals radii (3.5 and 3.4 Å, respective-ly [9]): S¹...C¹⁵ 3.288(4) Å to the molecule in position (x - 1, y + 1, z); C¹²...C¹⁵' 3.346(4), C¹³...C¹⁵' 3.375(4), C¹⁵'...C¹² 3.346(4), and C¹⁵'...C¹³ 3.375(4) Å to the molecule in position (1 - x, 2 - y, -z). The remaining intermolecular distances are greater by 0.05-0.3 Å than the sums of the van der Waals radii of the atoms.

EXPERIMENTAL

Infrared spectra were run on a UR-20 spectrometer using KBr discs. PMR spectra were obtained on Varian FT-80A (80 MHz) and Bruker WM-250 (250 MHz) instruments using solutions in DMSO-d. and TMS as reference. The purity of the compounds was verified by TLC using Silufol UV-254 plates and 3:5 acetone-hexane as solvent.

<u>6-Phenyl-3-cyanopyridine-2(1H)-thione (IIIa)</u>. To a suspension of 1.7 g (10 mmoles)(Ia) in 20 ml EtOH was added 0.4 ml AcOH and then 1 g (10 mmoles) cyanothioacetamide (II). The reaction mixture was brought up to boiling point, 0.2 ml AcOH added, and filtered. After 4 h the precipitate was separated, washed with EtOH and hexane and recrystallized from AcOH. Yield 1.2 g (57%) (IIIa), mp 254-255°C (decomp.). IR spectrum (KBr, v, cm⁻¹): 2224 (CN). PMR spectrum (DMSO-d., δ , ppm): 7.07 d (1H, H⁵); 8.06 d (1H, H⁴), J_{H⁴H⁵} = 7.5 Hz; 7.4 and 7.8 m (5H, C.H.); 14.02 (1H, NH). Found (%): C 67.82. H 3.94, N 13.12, S 14.87. Calculated for C.12HeN2S (%): C 67.90, H 3.80, N 13.20, S 14.60.

 $\frac{6-(4-\text{Chlorophenyl})-3-\text{cyanopyridine}-2(1\text{H})-\text{thione (IIIb)}}{(\text{IIIa}). \text{ Yield 38\%, mp 203-204°C (from AcOH). IR spectrum (KBr, <math>v$, cm^{-k}): 2226 (CN). PMR spectrum (DMSO-d_6, δ , ppm): 7.13 d (1H, H⁵); 8.10 d (1H, H⁴), $J_{\text{H}^4\text{H}^5} = 7.8$ Hz; 7.80 d and 7.54 d (1H, 4-ClC_6H_4), $^3\text{J} = 5.4$ Hz. Found (%): C 58.67, H 3.04, Cl 14.21, N 11.13, S 12.87. Calculated for C₁₂H₇ClN₂S (%): C 58.42, H 2.86, Cl 14.37, N 11.35, S 12.99.

 $\frac{6-(2,4-\text{Dimethoxyphenyl})-3-\text{cyanopyridine}-2(1\text{H})-\text{thione (IIIc)}}{(1112)} \text{ was prepared in a similar} way to (IIIa). Yield 47%, mp 196-197°C (from AcOH). IR spectrum (KBr, <math>v$, cm⁻¹): 2227 (CN). **PMR spectrum** (DMSO-d₅, δ , ppm): 3.81 s (3H, CH₃); 3.87 s (3H, CH₃); 6.50 m (3H, C₆H₃); 7.05 d (1H, H⁵); 8.03 d (1H, H⁴, J_H⁴H⁵ = 7.5 Hz); 13.96 s (1H, NH). Found (%): C 61.62, H 4.44, N 10.19, S 11.70. Calculated for C₁₄H₁₂N₂O₂S (%): C 61.75, H 4.44, N 10.29, S 11.77.

2,2'-Bis[6-(2,4-dimethoxyphenyl)-3-cyano-2-pyridyl] disulfide (IV). A suspension of 0.27 g (1 mmole) compound (IIIc) in 15 ml AcOH was heated to 50-55°C and filtered. The filtrate was left to stand for 4 days in air at 25°C and the precipitate removed and washed with



Fig. 1. Structure of the molecule of (IV). Dashed lines represent hydrogen bonds 0...H-C (only participating hydrogen atoms are shown).

TABLE 1. Coordinates of Atoms (×10⁵ for S, ×10⁴ for O, N, C, ×10³ for H)*

Atom	X	Y	z	Atom	X	Y	Z
31	5640 (8)	82737(6)	32855(5)	SI'	803(8)	70\$10(6)	26330(5)
ů.	8365 (2)	4615(1)	4117(1)	<u>ō</u> ,	3555(2)	10386(2)	-1260(1)
or l	6547(2)	1447(2)	$2861(2)^{-1}$	\tilde{O}^{2}	3577 (3)	14159(2)	2270(1)
Ň	3511(2)	6527(2)	3524(1)	$\tilde{N}^{1'}$	1405(2)	8725(2)	1244(1)
Nº I	2493(4)	10319(2)	4449(2) i	N^{2}	151(3)	4483(2)	(2) (1637
C ²	2914(3)	7589(2)	3590(1)	C²'	928(3)	7580(2)	1527(2)
Č3	3805(3)	8233(2)	4165(2)	C ³	1019(3)	6734(2)	1001(2)
Č,	5087 (3)	7699(2)	4465(2)	C','	1637(3)	7134(2)	139(2)
Č5	6030(3)	6588(2)	4297(2)	C°,	2139(3)	8320(2)	-162(2)
C6	5064(3)	5993(2)	3823(1)	C°'	2013(3)	9129(2)	400(2)
Č7	3070(4)	9403(2)	4325(2)	C ⁷	530(3)	5480(2)	1351(2)
C ⁸	5566(2)	4782(2)	-3613(1)	C ^s	2488(3)	10437(2)	168(1)
C?	7169(2)	4116(2)	3750(1)	C ⁹ ′	3214(3)	11049(2)	-643(2)
Cio	7509(3)	2996(2)	3518(2)	C10	3503(3)	12295(2)	-310(2)
C11	6285(3)	2510(2)	3140(2)	C'''	3266(3)	12943(2)	-167(2)
C12	4682(3)	3119(2)	3026(2)	C ¹²	2571(3)	12353(3)	649(2)
C ¹³	4359(3)	4233(2)	3250(2)	C ^{is}	2194(2)	11137(2)	797(2)
C1+	1:033(3)	-4011(2)	4189(2)	C^{11}	4172(3)	10913(0)	-2044(2)
C15	S214(4)	844 (0)	<u>2908(3)</u>	C ¹³	4226(4)	14830(C)	-1117(2)
Н÷	606(3)	810(2)	479(1)	$[H^{1}]$	-169(3)	661(2)	-25(1)
Н،	717(3)	625(2)	44 (2)	H ^a	256(3)	861(2)	-75(1)
H^{10}	865(2)	255(2)	360(1)	H ₁₀	405(2)	1267(2)	-136(1)
H12	381(3)	275(2)	275(1)	H:2	23(3)	1276(2)	114(1)
His	323(2)	470(2)	313(1)	H_{12}	171(2)	1076(2)	134(1)
Here	1032(3)	394(2)	361(1)	H14-1	376(3)	1162(2)	-2.6(2)
H14-2	1076(3)	459(2)	438(2)	H14-2	471(3)	1024(2)	-234(2)
H14-3	1005(3)	314(2)	461(2)	H ^{14.3}	559(3)	1123(2)	-100(2)
H15.1	816(4)	17(3)	261(2)	H15.1	434(3)	1367(2)	-104(2)
H ¹⁵⁻²	853(3)	50(2)	357(2)	H13-2	339(3)	1469(2)	= 100(2)
H15-3	903(3)	132(3)	266(2)	H12.	523(3)	1400(2)	-126(2)

*Isotope equivalent thermal parameters of nonhydrogen atoms (for H isotopes) can be obtained from the authors' laboratory.

AcOH, EtOH, and hexane. Yield 0.2 g (74%) (IV), mp 226-228°C (from AcOH). IR spectrum (KBr, ν , cm⁻³): 2220 (CN). PMR spectrum (DMSO-d₆, δ , ppm): 3.86 d (6H, (CH₃)₂); 6.52 m (3H, C₆H₃); 7.83 d (1H, H⁵) J_{H⁴H⁵} = 8.5 Hz; 7.96 d (1H, H⁴); 7.98 m (1H, C₆H₃ (signal partially overlapping H⁵). Found (%): C 61.79, H 3.94, N 10.42, S 11.74. Calculated for C_{2.0}H_{2.2}N₄O₄S₂ (%): C 61.98, H 4.09, N 10.33, S 11.82.

<u>2-Phenacylthio-6-phenyl-3-cyanopyridine (V)</u>. To a suspension of 0.84 g (4 mmoles) (IIIa) in 10 ml DMF, 2.2 ml 10% aqueous KOH was added with stirring followed by 0.8 g (4 mmoles) phenacyl bromide. The mixture was stirred for 20 min at 25°C, diluted with 5 ml water and the precipitate filtered off and washed with water. Yield 1.19 g (90%), mp 151-152°C (from toluene). IR spectrum (KBr, v, cm⁻¹): 1687 (CO), 2221 (CN). PMR spectrum (DMSO-ds, δ , ppm): 4.98 s (2H, CH₂); 7.2-8.2 m (10H, (C₆H₅)₂); 7.8 d (1H, H⁵); 8.18 d (1H, H⁴) (H⁵ and H⁴ signals partially overlapped C₆H₅ signals). Found (%): C 72.63, H 4.17, N 8.31, S 9.83. Calculated for C₂₀H₁₄N₂OS (%): C 72.71, H 4.27, N 8.48, S 9.70.

<u>2-Allythio-6-phenyl-2-cyanopyridine (VI)</u> was prepared in a similar way to (V), using allyl bromide as the alkylating agent. Yield 98%, mp 76°C (from hexane). IR spectrum (KBr, v, cm⁻¹): 2220 (CN). PMR spectrum (DMSO-d₆, δ , ppm): 4.01 d (2H, CH₂); 5.25 m (2H, CH₂); 6.0 m (1H, CH); 7.46 and 8.10 m (5H, C₆H₅); 7.81 d (1H, H⁵) 8.18 d (1H, H⁴) J_{H4H3} = 8.7 Hz. Found (%): C 71.27, H 4.17, N 11.12, S 12.82. Calculated for C₁₅H₁₂N₂S (%): C 71.40, H 4.80, N 11.10, S 12.70.

<u>3-Amino-2-benzoyl-6-phenylthiol[2,3-b]pyridine (VII)</u>. a) To a solution of 0.33 g (1 mmole) (V) in 4 ml DMF was added 0.5 ml 10% aqueous KOH. The reaction mixture was stirred for 2 h at 25°C, diluted with 5 ml water and the precipitate filtered off and washed with water, EtOH, and hexane. Yield 0.32 g (98%), mp 190-191°C (from n-butanol). b) To a suspension of 0.21 g (1 mmole) (IIIa) in 8 ml DMF was added 0.56 ml 10% aqueous KOH and 0.2 g (1 mmole) phenacyl bromide. The mixture was stirred for 10 min, 1 ml 10% aqueous KOH added, and stirring continued for 2 h at 25°C. It was then diluted with 5 ml water and the precipitate collected. Yield 0.26 g (86%), mp 190-191°C. The product was identical in terms of its IR spectrum with that obtained by method a). IR spectrum (KBr, v, cm⁻¹): 1596, 1600 (CO, δNH_2 , C=C), 3296, 3328, 3475 (NH₂). PMR spectrum (DMSO-d₆, δ , ppm): 7.4 and 8.2 m (10H, (C₆H₅)₂); 8.04 d (1H, H⁵); 8.37 d (1H, H⁴) J_{H4H5} = 9 Hz; 8.35 s (2H, NH₂). Found (%): C 72.58, H. 4.34, N 8.36, S 9.53. Calculated for C₂₀H₁₄N₂OS (%): C 72.41, H 4.27, N 8.48, S 9.20.

<u>3-Bromomethyl-5-phenyl-8-cyano-2,3,dihydrothiazolo[3,2-a]pyridinium bromide (VIII).</u> To a solution of 1.26 g (5 mmoles) (VI) in 20 ml dry chloroform, 0.26 ml (5 mmoles) bromine in 5 ml chloroform was added dropwise with stirring over 10 min. The mixture was stirred for 1 h at 25°C and the precipitate filtered off and washed with acetone. Yield 1.48 g (72%), mp 195°C (from nitromethane). IR spectrum (KBr, v, cm⁻¹): 2238 (CN). PMR spectrum (DMSO-de, δ , ppm): 3.49 and 3.64 m (2H, CH₂Br): 3.86 m and 4.35 m (2H, CH₂); 6.11 m (1H, CH); 7.73 m (5H, C₆H₅); 7.88 d (1H, H⁶); 8.96 d (1H, H⁷) J_{H⁶H⁷} = 9 Hz. Found (%): C 43.61, H 2.83, Br 38.97, N 6.54, S 7.62. Calculated for C₁₅H₁₂Br₂N₂S (%): C 43.71, H 2.94, Br 38.77, N 6.80, S 7.78.

<u>3-Bromomethyl-5-phenyl-8-cyano-2,3-dihydrothiazolo[3,2-a]pyridinium perchlorate (IX)</u>, a) To a mixture of 7 ml 70% perchloric acid, 7 ml acetic anhydride, and 40 ml AcOH was added 2.85 g (7 mmoles) (VIII). The mixture was heated for 10 min at 70-75°C, cooled to 25°C, diluted with 10 ml ether and the precipitate filtered off and washed with ether. Yield 2 g (66%), mp 236-239°C (from nitromethane). b) To a mixture of 7 ml 70% perchloric acid, 7 ml acetic anhydride and 40 ml AcOH was added 1.76 g (7 mmoles) (VI) followed by 0.37 ml (7 mmoles) bromine in 5 ml AcOH added dropwise over 20 min with stirring. The mixture was stirred 2 h at 25°C and then at bp for 1 h after which it was cooled, diluted with 20 ml ether, and the precipitate filtered off and washed with ether. Yield 1.7 g (56%), mp 236-239°C. The product was identical in terms of its IR spectrum with that obtained by method a). IR spectrum (KBr, v, cm⁻⁴): 2240 (CN). PMR spectrum (DMSO-d₆, δ , ppm): 3.34 d (2H, CH₂Br); 3.83 m and 4.28 m (2H, CH₂); 6.11 m (1H, CH); 7.69 m (5H, C₆H₅); 7.84 d (1H, H⁶); 8.96 d (1H, H⁷) J_H⁶H⁷ = 8.4 Hz. Found (%): C 41.60, H 2.68, Cl 8.12, Br 18.42, N 6.38, S 7.61. Calculated for C₁₅H₁₂Cl-BrN₂O₄S (%): C 41.74, H 2.80, Cl 8.21, Br 18.51, N 6.49, S 7.43.

X-ray diffraction analysis of 2,2'-bis[6-(2,4-dimethoxyphenyl)-3-cyano-2-pyridyl] disulfide (IV). Triclinic crystals, at 20°C a = 8.103(1), b = 11.056(1), c = 15.319(2) Å, a = 73.906(8), $\beta = 89.652(9)$, $\gamma = 83.825(8)$ °. V = 1310.6(2) Å³, d_{calc} = 1.38 g/cm³. Z = 2. C_{2s}-H₂₂N₄O₄S₂. Space group Pl. The intensities of 3228 independent reflections with I $\geq 2\sigma$ were measured on a Hilger-Watts 4-circle automatic diffractometer (λ MoK_a, graphite monochromator, $\theta/2\theta$ -scanning, $\theta_{max} = 30°$). Structure was interpreted by the direct method using the program MULTAN, revealing all nonhydrogen atoms, and refined by a full-matrix method of least squares in an anisotopic approximation for nonhydrogen atoms. All the hydrogen atoms were revealed from a difference series and refined isotropically. The final divergence factor R = 0.038, (R_w = 0.032). All the calculations were performed on an Eclipse S/200 computer running the INEXTL program [11]. The atomic coordinates are shown in Table 1.

Comparison of the x-ray diffraction data and the spectroscopic characteristic of (IV) and (IIIa-c) provides grounds for assuming that in the pyridinethiones (IIIa,b) the aryl substituent is located in the 6-position, not in the 4-position, of the pyridine ring, as was assumed on the basis of the proton NMR spectra [12], and comparison of the melting point of the pyridone obtained by oxidation of the corresponding 2-pyridyl sulfide with literature data [13].

CONCLUSIONS

1. Condensation of the sodium salts of 3-aryl-1-hydroxypropene-1-ones-3 with cyanoacetamide proceeds regioselectively with the formation of 6-aryl-3-cyanopyridine-2(1H)-thiones which are used in the synthesis of thieno[2,3-b]pyridine and thiazolo[3,2-a]pyridinium cations.

2. The structure of 2,2'-bis[6-(2,4-dimethoxypheny1)-3-cyanopyridine-2] disulfide has been established unequivocally by an x-ray diffraction study. The molecule is structured from two approximately planar fragments joined by a disulfide bridge with CSSC torsion angle = $83.5(2)^\circ$ and S-S bond length = 2.015(1) Å.

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SYNTHESIS OF α, α, ω -TRIHYDROPOLYFLUOROALKYL CHLOROPHOSPHATES BY THE REACTION BETWEEN α, α, ω -TRIHYDROPOLYFLUOROALKYL PHOSPHITES AND SULFURYL CHLORIDE

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Polyfluoroalkyl chlorophosphates are key compounds in the synthesis of practically useful derivatives of polyfluoroalkylphosphoric acids. Their preparation by alcoholysis of POCl₃ under severe conditions and in the presence of catalysts [1-4] results in the formation of mixtures of products. More efficient methods are the reactions of tris(polyfluoroalkyl) phosphites and polyfluoroalkyl dichlorophosphites [5] with chlorine [6] and nitrogen oxides [5, 7]. In order to obtain chlorophosphates, we here describe the reaction of α, α, ω -trihydropolyfluoroalkyl phosphites (and chlorophosphites) with the preparatively more convenient reagent sulfuryl chloride, which behaves towards three-coordinated phosphorus compounds as both a chlorinating agent [8, 9] and an oxidant [10].

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It has been found that $bis(\alpha, \alpha, \omega-trihydropolyfluoroalkyl)$ phosphites are chlorinated by sulfuryl chloride at 20-30°C in the same way as their hydrogen analogs [9], being uniquely converted into the $bis(\alpha, \alpha, \omega-trihydropolyfluoroalkyl)$ chlorophosphates (Ia-c).

$$(R_{\mathbf{P}}CH_{2}O)_{2}PHO + SO_{2}Cl_{2} \rightarrow (R_{\mathbf{P}}CH_{2}O)_{2}P(O)Cl + SO_{2} + HCl_{(1a-C)}$$

(ia-c)
$$R_{\mathbf{P}} = H(CF_{2}CF_{2})_{n}, n = 1(a), 2(b), (3c).$$

In an analogous reaction, α , α , ω -trihydropolyfluoroalkyl dichlorophosphites give only the oxidation products, α , α , ω -trihydropolyfluoroalkyl dichlorophosphates (IIa-c).

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